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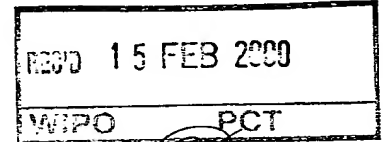
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Specification and Drawings, as originally filed, with Application for Patent Serial No:
2,,254,559, on November 20, 1998, by BAYER INC., assignee of Ahti August Koski, for
"Process for Hydrophobicizing Particles, and Their Use in Dispersions".

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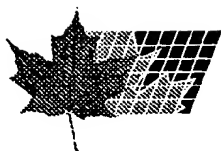
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(CIPO 68)

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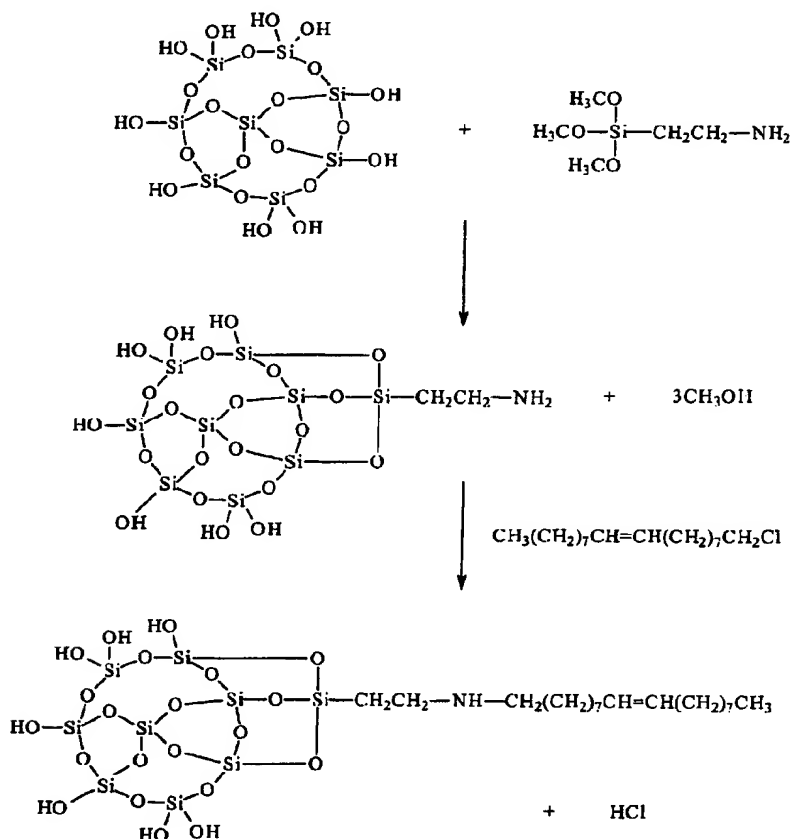
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(51) Int. Cl. ⁶ C09C 3/12, C08J 3/205, C09C 3/08, C08K 9/04, C09C 3/00

(54) **PROCEDE D'HYDROPHOBISATION DE PARTICULES ET
UTILISATION DE CELLES-CI DANS DES DISPERSIONS**

(54) **PROCESS FOR HYDROPHOBICIZING PARTICLES, AND
THEIR USE IN DISPERSIONS**



(57) Particles are hydrophobicized by in situ formation of a moiety containing amino and silane groups. The invention is particularly useful for treating hydrophilic inorganic particles. The treated particles can be used, for example, as a compound agent for polymers. The production and use of a predispersion or concentrate comprising a major amount of the treated particles and a binder is also described. Further, the production and use of masterbatch comprising a minor amount of the treated particles and a rubber is also described.

PROCESS FOR HYDROPHOBICIZING PARTICLES, AND
THEIR USE IN DISPERSIONS

In one of its aspects, the present invention relates to the hydrophobizing of particles, particularly inorganic water-insoluble compounds. In another of its aspects, the present invention also relates to an intermediate useful to produce the hydrophobicized particles. The treated particles are useful particularly, but not exclusively in the compounding of polymers, especially rubbers and plastics.

Raw polymers, either rubbers or plastics, rarely have the inherent physical or chemical properties in their pure state that are necessary to make useful articles. The polymers must thus be further compounded by mixing with additional ingredients or "additives". Polymer additives may include one or more of: secondary polymers; extender oils; fillers; antioxidants; coloring pigments, stabilizers, flame retardants, processing aids and other ancillary chemicals. For rubbers, this list may be extended to include curatives (vulcanizing agents) such as sulfur or organic peroxides; cure accelerators such as dibenzothiazyl disulphide (MBTS) and tetramethylthiuram disulfide (TMTD), as well as inorganic cure activators such as zinc oxide, lead monoxide (PbO, litharge), red lead (Pb₃O₄), and the like. Regardless of whether it is plastic or rubber properties in which improvement is sought, the selected additive materials must be mixed intimately with the polymer at the compounding stage (so as to obtain a homogeneous dispersion) in order for the maximum improvements to be realized. Conventionally, this mixing is usually accomplished on an open mill, in a mixing extruder or in an internal mixer (such as the Henschel, Welex or Banbury types) using one or more steps until the desired degree of dispersion is achieved.

Quite often, a satisfactory dispersion of the additive in the polymer is difficult to attain in a reasonable time, resulting in inhomogeneity which translates into unacceptable physical properties or appearance in the finished compound. To improve the dispersion, an extended mixing time or multi-stage mixing cycle must be employed which lowers productivity in the mixing plant and is thus undesirable.

Within the industry, it is known that mixing of inorganic chemicals such as the inorganic activators used in the rubber industry presents special difficulties in this

regard because of the inherent hardness and much higher viscosity of these chemicals relative to the polymer matrix.

One general method of facilitating mixing and dispersion of these inorganic materials into polymer compounds in the factory is to use a very fine particle size inorganic material. However, this inevitably generates dust during both the material
5 handling and mixing process and in many cases these dust particles are toxic or otherwise unacceptable from a worker health standpoint. Dust losses also change the ratio of the chemicals to the base polymer from what was originally intended; this may lead to poor processing or poor finished properties in the compound. In some
10 specific cases (i.e., with talc), very fine particles may act as a lubricant and actually contribute to poor mixing of the bulk, in this case by reducing the shear which is needed for dispersion. In other cases, especially where polar ingredients must be mixed into a non-polar polymer, agglomeration of the particles may occur during mixing, leading to undesirable inhomogeneity and unsatisfactory physical properties.

15 To mitigate the above problems, it is well known in the art to add the inorganic chemicals to the base polymer in a predispersed form, e.g., as fine particles bound in a low viscosity medium (or binder) such as polymer or oil, or combinations thereof with additional additives. This bound form of inorganic chemicals overcomes the dust problem in the rubber compounding plant and also greatly shortens the
20 dispersing time of the inorganic materials in the polymer compound, particularly if the binder is chemically similar to the base polymer and the viscosity of the pre-dispersion closely matches that of the rest of the compound. From a compounding standpoint, it is desirable to have the minimum amount of binder that will both facilitate dispersion and eliminate dusting during processing.

25 These types of "concentrates" or "dispersions" thus typically contain from about 50% to 95% by weight of the active inorganic chemical dispersed in a suitable binder (practically, this corresponds to a range of from 100 to 1900 parts by weight of inorganic chemical per 100 parts by weight of binder). Many such materials are commercially available from a number of suppliers to the rubber industries.

30 Non-limiting examples of such commercial polymer-bound materials used in the rubber industry are: RHENOGRAN® ZnO-85 (85 weight percent zinc oxide dispersed in an EPDM/EVA binder); POLY-DISPERSION® PLD-90 (90 weight

percent lead monoxide dispersed in polyisobutylene); RHENOGRAN® Pb₃O₄-90 (90 weight percent red lead oxide dispersed in EPDM/EVA), all available from Rhein-Chemie Corporation and Rhein Chemie Reinau GmbH.

Cheaper oil-based binders may also be used; while these address the dust problem, they do not offer as good or as rapid a dispersion as the presence of oil lowers the friction necessary to cause comminution of the inorganic materials during mixing. The presence of oil may also cause other changes in the physical properties (i.e., softening) or appearance (colour) which are undesirable. An example of the latter type of dispersion is Polydex™ PPD (ZnO) 75, a 75 weight percent blend of ZnO in a light process oil, available from Polychem.

In the plastics industry, it is often desired to modify the viscosity (i.e., the "melt index"), hardness, color, light-fastness and/or other properties of the base polymer in order to render it processible or suitable for its intended end-use application. Again, these additives (chemicals), in their pure form, may be added directly to the bulk plastic during the processing (compounding) phase; although, it is more customary to use the materials as concentrates in liquid or pellet form in order to obtain better dispersion and better control of the process. Again, these concentrates consist of a dispersion of fine particles of the additive in a suitable carrier or "binder" which may be similar or identical to the base polymer, or it may be another compatible polymer or a combination of polymers and oil. Also, other ingredients (e.g., soaps, compatibilizing agents and dispersing aids) may be included in the base of the binder. This concentrate form is used almost exclusively for introducing inorganic colorants into plastics where the high hardness and high melting point of the additives causes dispersion problems. Many companies currently supply inorganic and organic additive concentrates to the plastics industry; non-limiting examples of the latter materials include: ComPETe™, CELPRO™, Holoflake™, Hanna-FX™ (M.A. Hanna Color), BARKOLEN® (SPUR® a.s.), POLYPLUS™ (PolyTech South Inc.), CEK CONCENTRATES™, COLORPLAST™, CONCORDE™ (C.E.K. Concentrates) and the like.

Conventionally, these pre-dispersed forms of inorganic additives for use in the rubber and plastics industries have been produced by dry mechanical mixing or the ingredients – i.e., the additive in question is simply mechanically mixed with the

binder material. Unfortunately, this approach serves only to transfer the mixing and dust problems from the compounders plant to that of the supplier of the dispersion. Moreover, the relatively high percentage of inorganic material to binder desirable in these dispersions moreover requires long mixing times or the use of special high
5 energy mixing equipment (HIDM) which either lowers productivity or adds to the production costs. What would be most desirable is a dispersion manufacturing process that could be made essentially dust-free and moreover required little mixing energy to disperse the inorganic ancillary material in a polymeric binder.

A facile known method to prepare fine particle size materials from coarser
10 commercially available ones is by wet grinding, using either a ball, colloid or steam jet mill or other equipment as described under "Wet Grinding" in Ullmann's Encyclopedia of Industrial Chemistry Vol. B2 sec. 5-36, the contents of which are hereby incorporated by reference. As the fine particles produced are continuously in a wet state, they have little tendency to become airborne dust. However, the
15 concentration of the fine particles in the wetting medium is of necessity low in order to maintain the fluidity required for satisfactory grinding and thus the particles must be insoluble in the grinding medium. Where media other than water is employed during the size reduction process, additional hazards such as flammability must be taken into consideration. Further, the resulting dispersions typically require
20 concentration (i.e., solvent removal) before they can be further dispersed in a binder. Moreover, it is difficult to dry such fine particles without generating dust elsewhere in the process or without causing agglomeration (particle growth) during the drying step. Where possible, it would be preferable to produce masterbatches, dispersions and concentrates of these particles in suitable binders while the particles are still in a
25 finely divided wet state. It is also preferable for economy and safety perspectives that the grinding medium be water. An additional benefit of using water is that it is generally a non-solvent for most of the organic and inorganic additives which are sold as dispersions.

Further, number of prior art references teach how to make "masterbatches" of
30 fillers and dispersions of other chemicals in polymers by using fine particles dispersed in an aqueous state. For instance, Burke (United States patent 3,689,451, United States patent 3,689,452, United States patent 3,700,690, United States patent

3,716,513 and United States patent 3,840,382, the contents of each of which is hereby incorporated by reference) teaches how to use an aqueous dispersion of never-dried alkali silica pigment or a mixture of an aqueous dispersion of never-dried alkali silica pigment silica and carbon black to make a dispersion of these fillers in a matrix of rubbers at levels of <100 phr of filler (i.e., less than about 50% by weight of the filler dispersed in a rubber matrix). The rubbers must be used as solutions in water-immiscible solvents. Typically, large amounts of ancillary chemicals must also be employed to ensure transfer of the silica from the water suspension into the organic phase. In related patents (United States patent 3,686,219 and United States patent 3,694,398, the contents of each of which are hereby incorporated by reference) Burke teaches how to prepare similar dispersions from finely (aqueous) dispersed particles of silica by using the rubber in the form of a water emulsion – i.e., a latex. Nonetheless, all of the above Burke patents are restricted to the use of never-dried silica or combinations of never-dried silica and carbon black (i.e., conventional rubber fillers). The levels of the inorganic material in the finished dried masterbatch is moreover restricted to a low concentration and the binder is restricted to elastomers. To the knowledge of the inventor, no commercial masterbatches made by the Burke methods are currently available.

Contrary to the apparent commercial unavailability of silica masterbatches, masterbatches of carbon black and rubbers prepared from both water emulsions of polymers (i.e., the latex as resulting from emulsion polymerization) and solutions of polymers in hydrocarbons (i.e., as resulting when the polymer is soluble in the polymerization medium) have been available from several suppliers for a number of years (Copolymer Div. of DSM; Bayer Inc.; Goodyear, etc.). These masterbatches are usually prepared by grinding the carbon black in a wet aqueous state and then intensively mixing the black slurry with a solution-polymer “cement” or emulsion polymer latex, with or without added oil, followed by coagulation and drying. In all commercial products, the levels of black filler are <100 phr (i.e., less than about 50% by weight of the filler dispersed in a rubber matrix).

Where the polymer is available as an aqueous emulsion (i.e., latex), various methods are available for the incorporation of ancillary chemicals to form dispersions; the coprecipitation methods of Leo and Johansson (United States patent 4,110,240,

the contents of which are hereby incorporated by reference) may be used to prepare concentrates containing 80-99.5 wt% of the ancillary chemicals (excluding fillers), either organic or inorganic in the polymeric binder. Kanou et al. (United States patent 4,713,411, the contents of which are hereby incorporated by reference) detail a
5 different coprecipitation process to produce a pigment composition by using a special water-soluble polymeric binder which is then rendered insoluble by pH changes. However, many polymers, especially plastics, are prepared by a solution polymerization process and are not readily available in a latex form.

Despite previous efforts in the prior art, there remains a need for an efficient
10 manner of producing masterbatches, dispersions or concentrates of inorganic additive materials in a binder.

It is an object of the present invention to obviate or mitigate at least one of the above-mentioned disadvantages of the prior art.

It is another object of the present invention to provide a novel intermediate
15 material useful in the production of a relatively hydrophobic particulate material.

It is yet another object of the present invention to provide a novel process for treating particulate material to render it relatively hydrophobic.

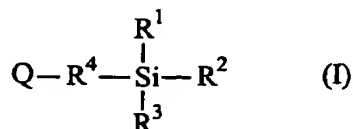
In copending International patent applications S.N. PCT/CA98/0499 [Koski #1] and S.N. PCT/CA98/0500 [Koski #2], the contents of which are hereby
20 incorporated by reference, there is taught a novel approach for producing masterbatches of polymers and particles. Generally, this approach, as taught in Koski #1, relates to initially rendering the particles hydrophobic to facilitate dispersion thereof in the polymer. Hydrophobicity is conferred to the particles by reacting the particles with a particular aminohydrocarbon silane compound. A particularly
25 preferred process to produce a useful such compound and a subset of novel such compounds are taught in Koski #2.

In the present application, there is taught an approach different to that taught in Koski #1 and Koski #2. Generally, the approach taught herein relates to in situ production of the functional moiety of the aminohydrocarbon silane compound on the
30 particulate material (i.e., as opposed to reaction of the pre-manufactured aminohydrocarbon silane compound and the particulate material).

Accordingly, in one of its aspects, the present invention provides a process for treating particles to render them hydrophobic, the process comprising the steps of:

- (i) contacting the particles with a compound of Formula I:

5



- 10 or an acid addition or quaternary ammonium salt thereof, in which:

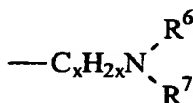
at least one of R^1 , R^2 and R^3 are hydroxyl or hydrolysable groups;

R^4 is a divalent group that is resistant to hydrolysis at the $\text{Si}-\text{R}^4$ bond;

Q is $\text{H}_2\text{N}-$ or $\text{X}-$, wherein X is an anion; and

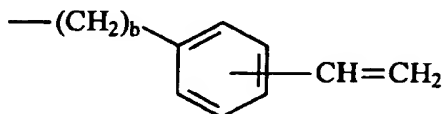
- (ii) contacting the particles with: (A) a compound of formula R^5-X if Q is $\text{H}_2\text{N}-$ in Formula I, or (B) a compound of formula R^5-NH_2 if Q is $\text{X}-$ in Formula I, wherein R^5 is selected from: hydrogen; a C_{1-40} alkyl; a C_{2-40} mono-, di- or tri-unsaturated alkenyl group; a C_6-C_{40} aryl group; a group of the formula:

20



- in which x is an integer from 2 to 10, R^6 and R^7 , which may be the same or different, are each selected from: hydrogen; C_{1-18} alkyl; C_{2-18} mono-, di- or tri-unsaturated alkenyl; phenyl; a group of formula:

30



wherein b is an integer from 1 to 10; a group of formula:



wherein c is an integer from 1 to 10, and R^8 and R^9 may be the same or different and are each selected from: hydrogen, C_{1-10} alkyl group or C_{2-10} alkenyl group, provided
10 that there is no double bond in the position alpha to the nitrogen atom; and a group of formula:



wherein r is an integer from 1 to 6 and d is an integer from 1 to 4.

Preferably, the present process of treating a particulate material is carried out in an aqueous solution, suspension or slurry, so that the product of the process is an
20 aqueous suspension or slurry of hydrophobicized mineral particles.

In one preferred embodiment, the suspension or slurry resulting from the present process, and containing the treated particles, is then mixed with a hydrocarbon solution of a polymer, and then dried to form a polymer-particle dispersion. Owing to the hydrophobicized nature of the treated particles, they are well dispersed in the
25 polymer. This preferred embodiment results in the production of a dispersion comprising the polymer and the treated particles. In this embodiment, the treated particles may be incorporated into a suspension without being isolated (i.e., separated from the suspension or slurry, and subsequently dried). This preferred embodiment results in the production of a dispersion comprising a polymer and a treated
30 particulate material (such as metal oxides and the like will be discussed in more detail hereinbelow), the dispersion having been prepared from a polymer solution without the need to utilize an aminohydrocarbon silane compound, per se.

Alternatively, the treated particulate material may be separated from the suspension or slurry, and subsequently dried for later use (i.e., before addition of the polymer solution).

In this specification, the terms "concentrate", "dispersion" and "pre-dispersion", when used in the context of the present invention, are intended to mean a composition comprising a particulate material (i.e., the additive(s) to be used for compounding purposes) and a binder therefor, wherein the particulate material is the major component of the composition - i.e., the composition comprises at least about 50 percent by weight particulate material. Preferably, the composition comprises from about 50 to about 95, more preferably from about 60 to about 95, even more preferably from about 70 to about 95, percent by weight particulate material. In this specification, the term "masterbatch", when used in the context of the present invention, is intended to mean a composition comprising a particulate material (i.e., the additive(s) to be used for compounding purposes) and a binder therefor, wherein the particulate material is the minor component of the composition - i.e., the composition comprises less than about 50 percent by weight particulate material. Preferably, the composition comprises from about 5 to about 50, more preferably from about 20 to about 45, even more preferably from about 30 to about 40, percent by weight particulate material.

Embodiments of the present invention will be described with reference to the accompanying drawing, in which:

Figure 1 illustrates an example of a first embodiment of the present process;

Figure 2 illustrates an example of a second embodiment of the present process; and

Figure 3 illustrates a schematic of a system useful to conduct the present process.

Throughout this specification, the invention is illustrated with reference to silica as the particle having surface hydroxyl groups, but it should be appreciated that the invention applies to the use of other such minerals, and the description understood accordingly. For example, carbon black may also be used. Further, carbon-silica dual phase fillers may also be used (e.g., Ecoblack CRX-2000™).

Thus, the present invention is particularly useful to the treatment of inorganic water insoluble compounds. Preferably the inorganic water insoluble compounds useful for treatment are those such compounds which contain oxygen, more preferably such compounds which also contain a metal. Preferably, the metal is selected from
5 Groups III-VIII of the Periodic Table of Elements. Examples of suitable groups of useful metal compounds may be selected from the group comprising oxides, hydroxides, borates, sulfates, carbonates, silicates, phosphates, chromates and the like. Non-limiting examples of suitable metal compounds may be selected from the group comprising titanium oxide, ferric oxide, hydrated ferric oxide, ferrous oxide, antimony
10 oxide, barium carbonate, zinc oxide, zinc borate, lead oxide (including red lead oxide), dibasic lead phosphite, lead silicate, tribasic lead sulfate and mixtures thereof. Other suitable metal compounds, especially those which are water insoluble or only slightly soluble in water, will be readily apparent to those of skill in the art base on the foregoing discussion. For example, a particularly preferred application of the present
15 invention is to hydrophobicize colorant or pigment particles which are typically used in the plastics industry. Non-limiting examples of suitable such particles may be selected from the group consisting of α -FeOOH (goethite), γ -FeOOH (lepidocrocite), α -Fe₂O₃ (hematite), γ -Fe₂O₃ (maghemite) and Fe₃O₄.

As stated above, the preferred particulate material for use herein is silica. In a
20 preferred embodiment, the treatment is carried out in an aqueous dispersion or slurry of the particles. Generally, the precise make up of the slurry is not particularly restricted provided that it is a mobile suspension. Practically, it is preferred that the slurry contain up to about 60% by weight, more preferably up to about 50% by weight, of particles to be treated. While the physical nature of the particles to be
25 treated is not particularly restricted, it is preferred that they have an average particle size in the range of from about 0.1 μ m to about 100 μ m, preferably from about 10 μ m to about 50 μ m, most preferably from about 10 μ m to about 25 μ m.

In the preferred embodiment, the treatment is carried out in an aqueous dispersion or slurry and the concentration of the aqueous dispersion or slurry of silica
30 particles may be between 1 and 30 percent by weight of silica in water, preferably between 5 and 25 percent by weight of silica in water and most preferably between 8 and 22 percent by weight of silica in water. Dried amorphous silica suitable for use in

accordance with the invention may have a mean agglomerate particle size between 1 and 100 microns, preferably between 10 and 50 microns and most preferably between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, of between 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, of between 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/II, of from 0 to 10 percent by weight. If filter cake is used, it may be made by any known means such as described in Ullmann's Encyclopedia of Industrial Chemical Vol A23 pages 642-643, VCH Publishers, ©1993. The filter cake has a preferred solids content of between 5 and 30 percent by weight, most preferably between 15 and 25 percent by weight, and it may be redispersed in water in accordance with the present process to give a silica concentration of between 5 and 20 percent by weight and most preferably between 8 and 12 percent by weight. It is preferred to use a filter cake.

If a never-filtered slurry prepared from the known reaction of a solution of alkali metal silicate with either mineral acid or carbon dioxide is used, it is preferred that the solids content of the never-filtered slurry be between 1 and 30, more preferably between 5 and 10, percent by weight of silica. The slurry temperature may be between 0° and 100°C if the process is conducted at atmospheric pressure or between 0° and 135°C if the operation is conducted in a pressure vessel. Most preferably, the process is conducted at atmospheric pressure in which case the preferred temperature is between 30° and 95°C and most preferably between 45° and 90°C.

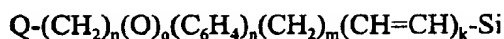
It is desirable that, prior to the addition to the silica particles of the compound of Formula I, the dispersion or slurry shall have a pH in the range from 6 to about 8, more preferably from about 6.8 to about 7.2. If necessary, the pH can be adjusted by addition of acid or alkali, for example mineral acid, alkali metal hydroxide, alkaline earth hydroxide, ammonium hydroxide and the like. These can be added as such or in aqueous solution.

In the compound of Formula I, it is preferred that all three of the groups R^1 , R^2 and R^3 are readily hydrolysable. Suitable groups R^1 include hydroxyl groups and hydrolysable groups of formula OC_pH_{2p+1} , where p has a value from 1 to 10. The alkyl chain can be interrupted by oxygen atoms, to give groups, for example, of
 5 formula CH_3OCH_2O- , $CH_3OCH_2OCH_2O-$, $CH_3(OCH_2)_4O-$, $CH_3OCH_2CH_2O-$, $C_2H_5OCH_2O-$, $C_2H_5OCH_2OCH_2O-$, or $C_2H_5OCH_2CH_2O-$. Other suitable hydrolysable groups include phenoxy, acetoxy, chloro, bromo, iodo, ONa, OLi, OK or amino or mono- or dialkylamino, wherein the alkyl group(s) have 1 to 30 carbon atoms.

R^2 and R^3 can take the same values as R^1 , provided that only one of R^1 , R^2 and
 10 R^3 is chloro, bromo or iodo. Preferably, only one or two of R^1 , R^2 and R^3 is hydroxyl or ONa, OLi or OK.

Non-limiting examples of groups R^2 and R^3 that are not hydrolysable include C_{1-10} alkyl, C_{2-10} mono- or diunsaturated alkenyl, and phenyl. R^2 and R^3 can also each be a group $-R^4-NR^5R^6$, discussed further below. It is preferred that R^1 , R^2 and R^3 are
 15 all the same and are CH_3O- , C_2H_5O- or C_3H_8O- . Most preferably they are all CH_3O- .

The divalent group R^4 is preferably such that $N-R^4-Q$ is of the formula:



20 in which k , m , n , o and p are all whole numbers. The order of the moieties between N and Q is not particularly restricted other than neither N or O should be directly bound to Si . The value of k is 0 or 1, the value of m is from 0 to 20 inclusive, the value of n is 0, 1 or 2, the value of o is 0 or 1 and the value of p is from 0 to 20 inclusive, with the provisos that the sum of the values of k , m , n , o and p is at least 1 and not more
 25 than 20 and that if o is 1, p is 1 or greater and the sum of k , m and n is 1 or greater, i.e. that the Si atom is linked directly to a carbon atom. There should be no hydrolysable bond between the silicon and Q atoms. Preferably, m is 3 and l , n , o and p are all 0, i.e., R^4 is $-CH_2CH_2CH_2-$.

The group R^5 is preferably a C_{8-20} monounsaturated alkenyl group, most
 30 preferably a C_{16-18} monounsaturated alkenyl group. R^6 is preferably hydrogen.

Without wishing to be bound by any particular theory or mode of action, it is believed that the mechanism of the present process can be illustrated with reference to Figures 1 and 2. In the embodiment illustrated in Figure 1, R¹, R² and R³ are each -OCH₃, R⁴ is -CH₂CH₂-, Q is -NH₂ and R⁵ is -CH₂(CH₂)₇(CH=CH)(CH₂)₇CH₃. In the embodiment illustrated in Figure 2, R¹, R² and R³ are each -OCH₃, R⁴ is -CH₂CH₂-, Q is -Cl and R⁵ is -CH₂(CH₂)₇(CH=CH)(CH₂)₇CH₃.

It is preferred that, for the specific compound of Formula I which is added, the equivalent balance (EB) should be calculated. The EB is used to determine whether mineral acid or alkali metal hydroxide, or solution thereof, should be added. The equivalent balance (EB) may be determined from the absolute value of the sum of the group values of salt anion (if present), R¹, R² and R³ and the magnitude of the sum of the group contributions of salt anion (if present), R¹, R² and R³ together with the weight added and the molecular weight of the compound of Formula I, according to the following scheme: The group contribution of salt anion for Cl or Br is -1, thus, if the salt anion is present, it is given a value of -1. The group contribution of each of R¹, R² and R³ is generally zero for all groups except as follows: if the group is CH₃COO, Cl or Br, in which case it is -1, or if it is amine (including an imine), ONa, OK or OLi in which case it is +1. If the sum of the group contributions for the salt anion (if present), R¹, R² and R³ is zero, no adjustment with mineral acid or alkali metal hydroxide (or solutions thereof) is necessary. If the sum of the group values is a positive integer, adjustment with mineral acid is desirable, and if it is negative, adjustment with alkali metal hydroxide is desirable.

For example, where R¹=OCH₃, R²=CH₃, R³=Cl and salt anion=Br, the sum of the group values (g.v.) is:

$$\sum = (\text{g.v. OCH}_3) + (\text{g.v. CH}_3) + (\text{g.v. Cl}) + (\text{g.v. Br}) = (0) + (0) + (-1) + (-1) = -2$$

The negative sign in front of the sum indicates adjustment with alkali metal hydroxide is desirable. The number of equivalents of alkali required is given by the equivalent balance (EB) which includes the absolute value of the sum of the group contributions ($|\sum|$) as a scaling factor:

$$EB = \frac{\sum |x| \times \text{weight in grams of the chemical added}}{\text{molecular weight of the added chemical}}$$

In continuing the example, if a process according to the present invention were
 5 scaled so as to require 6,000 grams of a chemical of Formula I with a molecular
 weight of 350 grams and the sum of the group values gave -2, EB would be calculated
 as follows:

$$EB = -2 \times 6000/350 = -34.28 \text{ gram-equivalents}$$

10

Thus, in this example, 34.28 gram-equivalents of alkali metal hydroxide would
 be added. Sodium hydroxide is the preferred alkali metal hydroxide. The weight of
 sodium hydroxide would be:

$$15 \quad \text{Weight} = (EB) \times (\text{Equivalent Weight of NaOH}) = 34.28 \times 40.0 = 1371.2 \text{ grams}$$

The preferred technique according to the invention is to dissolve the alkali
 metal hydroxide or mineral acid in water so as to obtain a concentration in the range
 of from about 5 to about 25 percent by weight, most preferably in the range of from
 20 about 5 and about 10 percent by weight prior to adding the solution to the slurry.

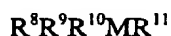
In a preferred embodiment, the present process comprises the further step of
 reacting the hydrophobicized particles with a coupling agent. This is particularly
 advantageous when the hydrophobicized particles are to be dispersed into rubber that
 is intended to be vulcanized and used, for instance, in tires. In this embodiment, it is
 25 preferred that the present process is conducted using a stoichiometric amount of the
 compound of Formula I which is less than that required to react with substantially all
 of the pendant moieties on the surface of the particles being treated. This will
 facilitate reaction of the treated particles as described and illustrated (see specifically
 Figures 1-4) in Koski #1.

30 Suitable coupling agents include those described in United States patent
 4,704,414, published European patent application 0,670,347A1 and published German
 patent application 4435311A1, the disclosures of each of which are incorporated by
 reference. One suitable coupling agent is a mixture of bis[3-(triethoxysilyl)propyl]-

monosulfane, bis[3-(triethoxysilyl)propyl]disulfane, bis[3-(triethoxysilyl)propyl]-
 trisulfane and bis[3-(triethoxysilyl)propyl]tetrasulfane and higher sulfane homologues
 - for example, coupling agents available under the trade names Si-69 (average sulfane
 3.5) and Silquest™ A-1589 or Si-75 (average sulfane 2.0). In the past, achieving a
 5 good balance between the coupling agent and particles, such as silica, without
 scorching or premature curing has proven difficult. In accordance with the invention,
 if particles, particularly silica particles, are being treated to render them hydrophobic
 for use in rubber which is subsequently to be vulcanized, it is possible to include a
 step of adding a coupling agent in the process of the invention, so that the coupling
 10 agent becomes attached to the surface of the hydrophobicized mineral particles and
 becomes dispersed in the rubber with the mineral particles.

The coupling agent may be added after any addition of mineral acid or alkali
 metal hydroxide that is indicated by the calculation of the EB. Non-limiting examples
 of suitable coupling agents include compounds of formula:

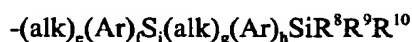
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in which at least one of R^8 , R^9 and R^{10} , preferably two of R^8 , R^9 and R^{10} and most
 preferably R^8 , R^9 and R^{10} , are hydroxyl or hydrolysable groups. The groups R^8 , R^9
 20 and R^{10} are bound to the atom M, which is silicon, titanium or zirconium. The group
 R^8 may be hydroxyl or OC_pH_{2p+1} where p is from 1 to 10 and the carbon chain may
 be interrupted by oxygen atoms, to give groups, for example, of formula CH_3OCH_2O- ,
 $CH_3OCH_2OCH_2O-$, $CH_3(OCH_2)_4O-$, $CH_3OCH_2CH_2O-$, $C_2H_5OCH_2O-$,
 $C_2H_5OCH_2OCH_2O-$ or $C_2H_5OCH_2CH_2O-$. Alternatively R^8 may be phenoxy. If M is
 25 titanium or zirconium, R^8 may be the neopentyl(diallyl)oxy group, but not if M is
 silicon. The group R^9 may be the same as R^8 . If M is silicon, R^9 may also be a C_{1-10}
 alkyl group, a phenyl group, or a C_{2-10} mono- or diunsaturated alkenyl group. If M is
 titanium or zirconium, R^9 may be the neopentyl(diallyl)oxy group, but not if M is
 silicon. Further, R^9 may be the same as the group R^{11} described below.
 30 R^{10} may be the same as R^8 , but it is preferred that R^8 , R^9 and R^{10} are not all
 hydroxyl. If M is silicon, R^{10} may also be C_{1-10} alkyl, phenyl, C_{2-10} mono- or
 diunsaturated alkenyl. If M is titanium or zirconium, R^{10} may be the

neopentyl(diallyl)oxy group, but not if M is silicon. Further R^{10} may be the same as the group R^{11} described below.

The group R^{11} attached to M is such that it may participate in a crosslinking reaction with unsaturated polymers by contributing to the formation of crosslinks or by otherwise participating in crosslinking. In the case where M is silicon, R^{11} may have one of the following structures: R^{11} may represent the allyl group $-H_2CCH=CH_2$, the vinyl group $-CH=CH_2$, the 5-bicycloheptenyl group or the group described by



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where R^8 , R^9 and R^{10} are the same as previously defined, alk is a divalent straight hydrocarbon group having between 1 and 6 carbon atoms or a branched hydrocarbon group having between 2 and 6 carbon atoms, Ar is either a phenylene $-C_6H_4-$, biphenylene $-C_6H_4-C_6H_4-$ or $-C_6H_4-OC_6H_4-$ group and e, f, g and h are either 0, 1 or 2 and i is an integer from 2 to 8 inclusive with the provisos that the sum of e and f is always 1 or greater than 1 and that the sum of g and h is also always 1 or greater than 1. Alternately, R^{11} may be represented by the structures $(alk)_e(Ar)_fSH$ or $(alk)_e(Ar)_fSCN$ where e and f are as defined previously. Moreover, it is possible for R^{11} to have the structure

20



wherein k, m, n and o and p are all whole numbers and R^{13} represents the acryloxy $CH_2=CHCOO-$ or the methacryloxy $CH_2=C(CH_3)COO-$ group. Further, the value of k may be 0 or 1, m may be from 0 to 20 inclusive, n may be between 0 and 2, o may be 0 or 1, and p may be from 0 to 20 inclusive, with the provisos that the sum of k, m, n and o is at least 1 and not greater than 20, and that if n is 1 or 2 or o is 1, p is 1 or greater. It is most preferable that $m=3$ and k, n, o and p are all 0.

Preferably, R^8 , R^9 and R^{10} are all either OCH_3 , OC_2H_5 or OCH_2CH_3 groups and most preferably all are OCH_3 groups. It is most preferred that the coupling agent is bis[3-(trimethoxysilyl)propyl]tetrasulfane (Si-168). The amount of coupling agent to

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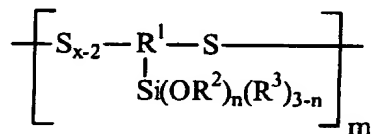
add is optional; levels between 2 and 10 percent by weight of the silica in the slurry (dry basis) are preferred. The dispersion of the chemical may be effected by mixing.

Non-limiting illustrative examples of other coupling agents include the following: bis[(trimethoxysilyl)propyl]disulfane (Si-166),

- 5 bis[(triethoxysilyl)propyl]disulfane (Si-266), bis[2-(trimethoxysilyl)ethyl]-tetra-sulfane, bis[2-(triethoxysilyl)ethyl]trisulfane, bis[3-(trimethoxysilyl)propyl]disulfane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldi-ethoxysilane, 3-mercaptoethylpropylethoxymethoxysilane, 1,3-bis(3-acryloxypropyl)tetramethoxy-disiloxane, acryloxypropylmethyldimethoxysilane, 3-methacryloxypropyl-
- 10 trimethoxysilane, allyltrimethoxysilane, diallyldiethoxysilane, 5-(bicyclo-heptenyl)triethoxysilane, 5-(bicycloheptenyl)methylmethoxyethoxysilane, isopropoxytriacyltitanate, diisopropyldimethacryltitanate, diethoxydi(3-mercaptopropoxy)zirconate, triisopropoxy-(2-mercaptoethoxy)zirconate, and di[neopentyl(diallyl)oxy]-di(3-mercaptopropoxy)-zirconate.

- 15 Other preferred coupling agents include those disclosed in published German patent application 4435311A1 mentioned above. On pages 2 and 3, there is disclosure of oligomers and polymers of sulphur containing organooxysilanes of the general formula:

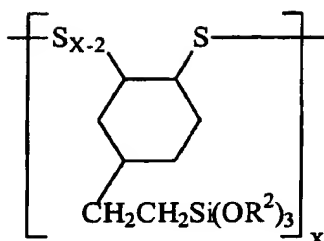
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- 25 in which R^1 is a saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon group that is at least trivalent and has from 2 to 20 carbon atoms, provided that there are at least two carbon-sulphur bonds, R^2 and R^3 , independently of each other, are saturated or unsaturated, branched or unbranched, substituted or unsubstituted hydrocarbon groups with 1 to 20 carbon atoms, halogen,
- 30 hydroxy or hydrogen, n is 1 to 3, m is 1 to 1000, p is 1 to 5, q is 1 to 3 and x is 1 to 8.

Preferred compounds are of the general formula

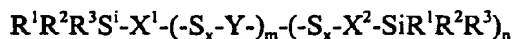
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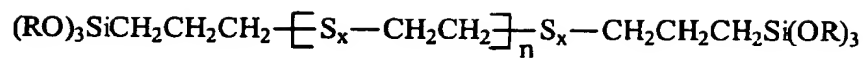
wherein R^2 , m and x have the meanings given above, and R^2 is preferably methyl or ethyl. These compounds disclosed in German patent application 4435311 A1 are preferred coupling agents for use in the present invention.

Also preferred for use in this invention are coupling agents disclosed in the abovementioned published European patent application 0,670,347A1, which discloses coupling agents of the general formula:

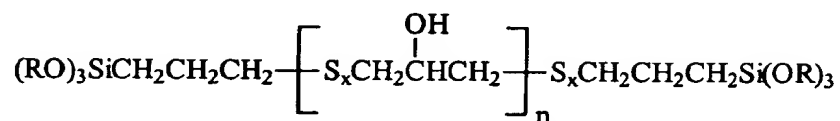


20 in which R^1 , R^2 and R^3 are the same or different and are C_{1-8} alkyl, C_{1-8} alkoxy, phenyl or phenoxy, provided that at least one of R^1 , R^2 and R^3 is an alkoxy or phenoxy group. X^1 and X^2 are the same or different and are divalent linear or branched, optionally unsaturated C_{1-12} alkyl groups, Y is a di-, tri- or tetravalent linear, branched or cyclic C_{1-18} alkyl group that is optionally unsaturated and is optionally substituted by C_{6-12} aryl, C_{1-8} alkoxy or hydroxy groups and which can be interrupted by oxygen, sulphur or nitrogen atoms or aromatic C_{6-12} aryl groups, or Y is a C_{6-12} aryl or heteroaryl group, 25 m is an integer from 1 to 20, n is an integer from 1 to 6 and x is an integer from 1 to 6.

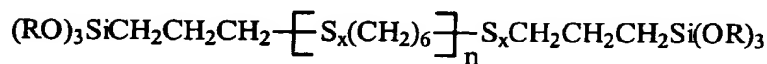
Particularly preferred coupling agents are those of the following general formulae:



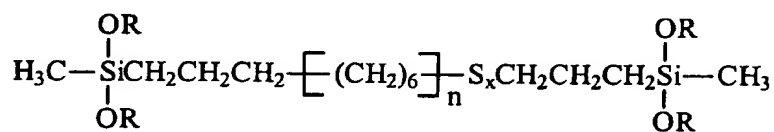
in which R = -CH₃ or -C₂H₅, x=1-6 and n=1-10;



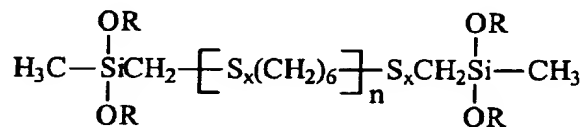
in which R = -CH₃ or -C₂H₅, x = 1-6 and n = 1-10;



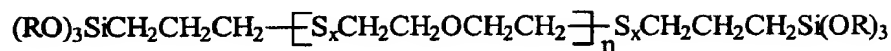
in which R = -CH₃, -C₂H₅ or -C₃H₇, n = 1-10 and x = 1-6;



in which R = -CH₃, -C₂H₅ or -C₃H₇, n = 1-10 and x = 1-6;

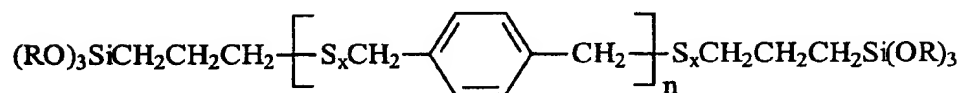


in which R = -CH₃, -C₂H₅ or -C₃H₇, n = 1-10 and x = 1-6;

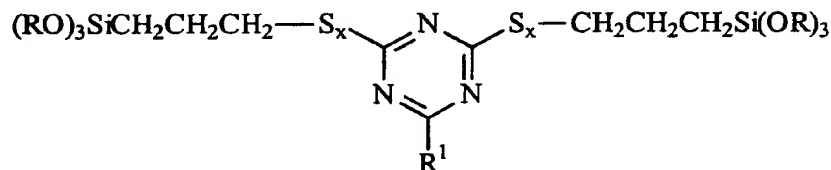


in which R = -CH₃, -C₂H₅, -C₃H₇, n = 1-10 and x = 1-6;

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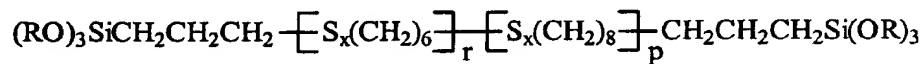


10 in which R = -CH₃, -C₂H₅ or -C₃H₇, n = 1-10 and x = 1-6;



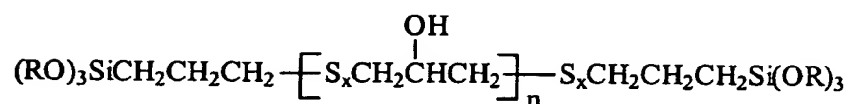
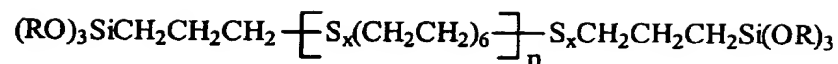
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in which R = -CH₃, -C₂H₅, or -C₃H₇; R¹ = -CH₃, -C₂H₅, -C₃H₇, -C₆H₅, -OCH₃, -OC₂H₅,
 20 -OC₃H₇ or -OC₆H₅, n = 1-10 and x = 1-8; and



in which R = -CH₃, -C₂H₅ or -C₃H₇, r+p = 2-10 and x = 1-6.

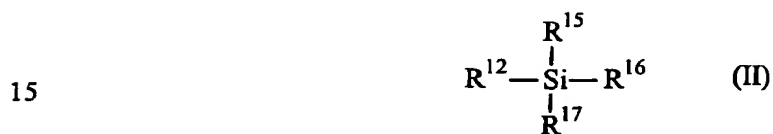
Especially preferred are coupling agents of the formulae:



5 in which x is 1-6 and n is 1-4.

Alternatively, the functionality of a coupling agent can be formed on the surface of the particles *in situ* using the approach described in Canadian patent application • (Bayer Ref: POS-1060) filed on even date herewith, the contents of which are hereby incorporated by reference.

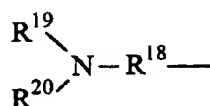
10 In a preferred embodiment of the present process, the product of the present process is further reacted with a compound of Formula II:



in which:

20 R^{15} , R^{16} and R^{17} have the same definitions as R^1 , R^2 and R^3 in Formula I hereinabove; and

R^{12} is selected from the group comprising a C_{8-40} alkyl group or a C_{8-40} mono-, di- or tri-unsaturated alkenyl group, either of which can be interrupted by one or more aryl groups, preferably phenyl groups; a group of formula:



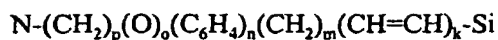
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or an acid addition or quaternary ammonium salt thereof in which R^{18} is a divalent group resistant to hydrolysis at the Si- R^{18} bond, R^{19} is selected from the group comprising hydrogen, a C_{1-40} alkyl group, a C_{2-40} mono-, di- or tri-unsaturated alkenyl group, a substituted aromatic group, for example the phenylene group $-(\text{C}_6\text{H}_4)-$, the biphenylene Group $-(\text{C}_6\text{H}_4)-(\text{C}_6\text{H}_4)-$, the $-(\text{C}_6\text{H}_4)-\text{O}-(\text{C}_6\text{H}_4)-$ group or the naphthylene group, $-(\text{C}_{10}\text{H}_6)-$, the aromatic group being unsubstituted or substituted by a C_{1-20} alkyl or C_{2-20} mono-, di- or tri-unsaturated alkenyl group; and R^{20} may be any of the groups defined for R^{19} , with the provisos that R^{19} and R^{20} do not have a tertiary carbon atom adjacent to the nitrogen atom and that at least one of R^{19} and R^{20} has a carbon chain at least 8 carbon atoms in length uninterrupted by any heteroatoms.

In this embodiment, it is preferred that the present process is conducted using a stoichiometric amount of the compound of Formula I and coupling agent (if used) which is less than that required to react with substantially all of the pendant moieties on the surface of the particles being treated. This will facilitate reaction of the treated particles as described and illustrated (see specifically Figures 1-4) in Koski #1.

Preferably, R^{18} is a $\text{C}_1\text{-C}_{40}$ saturated or unsaturated group (e.g., alkenyl, aryl, cycloalkyl and the like).

In this preferred embodiment, again, it is preferred that the particulate filler material, more preferably a mineral filler, is in the form of an aqueous slurry or a dispersion, and the compound of Formula II is added to the slurry or dispersion under intense mixing. In the compound of Formula II the possible and preferred values for R^{15} , R^{16} and R^{17} are the same as the possible and preferred values for R^1 , R^2 and R^3 that are discussed above in relation to Formula I. If R^{12} is an amino group of formula $-\text{R}^{18}-\text{NR}^{19}\text{R}^{20}$, preferred values for R^{18} are such that N- R^{18} -Si includes groups of the formula:



in which k is 0 or 1, m is 0 to 20 inclusive, n is 0, 1 or 2, o is 0 or 1 and p is 0 to 20 inclusive, provided that the sum of k, m, n, o and p is at least 1 and not greater than 20, and further provided that if o is 1, p is also 1 or greater, and the sum of k, m and n is 1 or greater. The order of the moieties between N and Si is not particularly restricted other than neither N or O should be directly bound to Si. There should be no hydrolysable group between the silicon and nitrogen atoms. Preferably k, n, o and p are all 0 and m is 3, i.e. R¹⁸ is -CH₂CH₂CH₂-.

R¹² may be a moiety containing at least one primary, secondary, or tertiary amine nitrogen. In this case the amino group bonded to R¹⁸- is given by the formula -NR¹⁹R²⁰. R¹⁹ may be a H or a C₁₋₄₀ alkyl group or a C₂₋₄₀ mono-, di- or tri-unsaturated alkenyl group. R¹⁹ may also be a C₁₋₂₀ alkyl-substituted or C₂₋₂₀ alkenyl-substituted aromatic group. The aromatic group may be, for example, the phenylene group -(C₆H₄)-, the biphenylene group -(C₆H₄)-(C₆H₄)-, the -(C₆H₄)-O-(C₆H₄)- group, or the naphthylene group -(C₁₀H₆)-. R²⁰ may be one of the same groups as R¹⁹ with the further proviso that at least one of R¹⁹ and R²⁰ must contain a continuous carbon chain of at least 8 carbons in length, uninterrupted by any heteroatoms.

As stated above, if R¹⁹ and R²⁰ are other than hydrogen, the carbon atom attached to the nitrogen atom is not tertiary. Preferably the carbon atom attached to the nitrogen atom is primary, i.e., -CH₂-.

It is preferred that R¹⁹ is a mono-unsaturated alkenyl group of 12-20 carbons in length and most preferable that R¹⁹ is a monounsaturated alkenyl group of 16 to 18 carbons in length. It is most preferable also that R²⁰ is H.

Alternatively, R¹² may be a moiety which contains a mineral acid salt or a quaternary ammonium salt of an amine. The formula of R¹² may thus be described by the extended formula -R¹⁸-NR¹⁹R²⁰.R²¹X wherein -R¹⁸-, R¹⁹ and R²⁰ are as previously defined and R²¹ may be a H, or a C₁₋₄₀ alkyl or C₂₋₄₀ mono-, di- or tri-unsaturated alkenyl group and X is an anion, preferably Cl or Br, although sulphate can be used.

If the compound of Formula II is used, there is the further proviso that at least one of R¹⁹ and R²⁰ must contain a continuous carbon chain of at least 8 carbons in length, uninterrupted by any heteroatom. It is preferred to use an amine salt where R¹⁹

is a mono- or di-unsaturated alkenyl group of 12-20 carbons in length and most preferably that R¹⁹ is a mono- or di-unsaturated alkenyl group of 16 to 18 carbons in length. It is most preferable also that R²⁰ is H and that R²¹ is H and X is chlorine. The preferred hydrophobicizing agent of Formula II is N-oley1-N-(3-
5 trimethoxysilyl)propyl ammonium chloride.

Preferably, the amount of the hydrophobic compound of Formula II to add is generally between 0.5 and 20 percent by weight of the weight of the particles (preferably mineral particles such as silica) in the slurry (dry basis), and is inversely proportional to the particle size of the silica particles. The compound may be added to
10 the slurry in its natural state, either as a liquid or a solid. However, to facilitate dispersion, it is preferred, where possible, to add the compound as a liquid. If the melting point of the compound is below 95°C, it is preferred to add it to the slurry in a molten state at a temperature at least 5°C above the melting point, provided the temperature of the compound in the liquified state does not exceed 100°C and
15 provided that the compound does not decompose under these conditions. If the melting point exceeds 95°C, it is most preferred to use a solvent. Suitable solvents are alcohols containing 1 to 5 carbon atoms and most preferably those containing 1 to 3 carbon atoms, that is to say methanol, ethanol, n-propanol or isopropanol. If the compound of Formula II is an alkoxysilane, most preferably the alkoxy group of the
20 solvent alcohol will be the same as the alkoxy group of the alkoxysilane. For example, if the compound of Formula II is a methoxysilane, the preferred solvent is methanol. The concentration of the compound in the solvent may be from 10 to 90 percent by weight and most preferably between 25 and 75 percent by weight and most preferably 50 percent by weight. Preferably, the solution is prepared and added to the
25 slurry at a temperature between a lower limit of 0°C and an upper limit which is the lower of at least 10°C below the boiling point of the solvent and 95°C.

After the addition of the hydrophobic compound of Formula II which is added, the equivalent balance (EB) should be calculated to determine how much, if any, mineral acid or alkali metal hydroxide (or solutions thereof) to add. The equivalent
30 balance (EB) may be determined from the absolute value of the sum of the group values of salt anion (if present), R¹⁵, R¹⁶ and R¹⁷ and the weight added, and the molecular weight of the compound, according to the following scheme: The group

contribution of the salt anion (salt anion) for Cl or Br is -1, thus if salt anion is present it is given a value of -1. The group contribution of each of R^{15} , R^{16} and R^{17} is generally zero for all groups except as follows: if the group is $\text{CH}_3\text{COO}^\ominus$, Cl^\ominus or Br^\ominus , in which case it is -1, or if it is amino, ONa, OK, or OLi in which case it is +1. If the sum of the group contributions for salt anion (if present), R^{15} , R^{16} and R^{17} is zero, no adjustment with mineral acid or alkali metal hydroxide (or solutions thereof) is necessary. If the sum of the group values is a positive integer, adjustment with mineral acid is desirable, and if it is negative, adjustment with alkali hydroxide is desirable.

For example, where $R^{15}=\text{OC}_2\text{H}_5$, $R^{16}=\text{OCH}_3$, $R^{17}=\text{CH}_3$ and salt anion= Cl , the sum Σ of the group values (g.v.) is:

$$\Sigma = (\text{g.v. OC}_2\text{H}_5) + (\text{g.v. OCH}_3) + (\text{g.v. CH}_3) + (\text{g.v. Cl}) = (0) + (0) + (0) + (-1) = -1.$$

The negative sign in front of the sum indicates adjustment with alkali metal hydroxide is required. The number of equivalents of alkali required is given by the equivalent balance (EB) which includes the absolute value of the sum of the group contributions ($|\Sigma|$) as a scaling factor.

$$\text{EB} = \frac{|\Sigma| \times \text{weight in grams of the compound added}}{\text{molecular weight of the added chemical.}}$$

In continuing the example, if a process according to the present invention were scaled so as to require 3450 grams of a compound of Formula II with a molecular weight of 466 grams and the sum of the group values gave -1, EB would be calculated as follows:

$$\text{EB} = |-1| \times 3450/466 = 7.4 \text{ gram-equivalents.}$$

Thus, in this example, 7.4 gram-equivalents of alkali metal hydroxide would be added. Sodium hydroxide is the preferred alkali metal hydroxide. The weight of sodium hydroxide added would be:

Weight = (EB)x(Equivalent Weight of NaOH) = 7.4 x 40.0 = 296 grams.

The preferred technique according to the invention is to dissolve the alkali hydroxide or mineral acid in water so as to obtain a concentration between 5 and 25% by weight and most preferably between 5 and 10% by weight prior to adding the solution to the slurry. The temperature of the solution may be from 0° to 100°C under atmospheric pressure, or if a pressure vessel is used for preparation of the solution, it may be from 0° to 130°C. It is preferred that the temperature of the solution be within 10°C of the solution of the slurry. The dispersion of the solution in the slurry is effected by mixing.

The product of the present process described thus far relates an aqueous slurry or dispersion of hydrophobicized particles (i.e., it has not yet been contacted with a polymer or other substrate to be filled), which can be used as such or can be filtered and dried.

The hydrophobicized particles may be used as a compounding agent in a multitude of materials including, but not limited to, the following: polymers, alkyd paints, toners such as those used in photocopiers, modified plastics and rubber vulcanizates.

In a preferred embodiment of this invention the hydrophobicized silica, in the aqueous dispersion or slurry, is incorporated into a polymer, for example an elastomer to form a rubber masterbatch. It is particularly preferred that the hydrophobicized silica shall have been treated with a coupling agent, for example Si-69, Si-168 or Silquest RC-2, as discussed above. The slurry is mixed with a hydrocarbon or other solution of the elastomer. Preferably, the solvent in which the elastomer is dissolved is immiscible with, or mostly immiscible with, water to form a preblend. This elastomer solution may be made by dissolving the solid elastomer in a solvent, or it may be the solution resulting from the polymerisation of monomers in the solvent. The elastomer may be a hydrocarbon rubber, a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation. Other suitable polymers include, but are not limited to butyl rubber (IIR), halogenated butyl rubber (HIIR), cis-1,4-polyisoprene rubber (IR), ethylene-propylene-diene monomer (EPDM) rubber, ethylene-propylene monomer

(EPM) rubber, styrene-butadiene rubber (SBR), polybutadiene rubber (BR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), HSRE, natural rubber (NR), polystyrene (PS), chloroprene¹ rubber (CR), ethylene-vinyl acetate (EVM) rubber, epichlorohydrin (ECO) rubber, chlorinated polyethylene, silicone rubber (Q), urethane rubber (AU EU), acrylonitrile-butadiene-styrene (ABS) polymers and the like. Suitable solvents include but are not limited to cyclohexane, hexane, benzene, toluene and pentane. Optionally, processing oil and antioxidants may be added to the hydrocarbon solution prior to mixing with the slurry, or they may be added after mixing the slurry and the elastomer solution.

10 The viscosity of the final elastomer solution, sometimes referred to as an elastomer cement, containing the optional ingredients is preferably such that it closely matches the viscosity of the silica slurry and is generally between 1,000 and 50,000 centipoise. The temperature of the elastomer solution is preferably the same as that of the slurry and the amount of cement that is added is such that the final masterbatch
15 may contain from 5 to 250 parts of silica per hundred parts of elastomer, preferably from 35 to 100 parts of silica per hundred parts of elastomer, most preferably from 60 to 80 parts of silica per hundred parts of elastomer.

The elastomer cement and, optionally, oil and antioxidants, is mixed with the silica slurry until the mixture becomes homogeneous and the milky colour of the silica
20 slurry disappears to form a preblend. A small amount of water may separate at this stage.

If not added previously, or if additional amounts are desired, oil and antioxidants may be added next and the mixing continued further until the oil and antioxidant become incorporated in the continuous phase.

25 Any water which separates from the preblend may be removed, discarded or recycled for silica slurry make-up by stopping the agitator for a suitable period and allowing the water phase to accumulate in the bottom of the mixing tank from which it may be drained prior to proceeding with the next step. Agitation is preferably restarted after the water layer is removed.

¹Also known as NeopreneTM.

If antioxidants and processing oil were not previously added, or if additional amounts are desired, they may be added at this stage and stirring continued until the preblend is again homogeneous.

5 The preblend is then added to water heated to a temperature equal to, or preferably higher than the boiling point of the solvent used for the elastomer cement so as to remove the solvent and produce a masterbatch coagulum in the form of a crumb suspended in water. The preferable temperature of the water prior to addition of the preblend is between 50° and 100°C, most preferably between 90° and 95°C, and the preblend is added at a rate so as to maintain a so-fixed or reasonably so-fixed
10 water temperature throughout the coagulation. The agitation is set sufficiently high so as to maintain the crumb in a suspended state within the water but not so high as to cause the crumb to subdivide into particles smaller than approximately 5 millimeters.

The solvent may be recovered from the coagulator by recondensing the vapours. The material containing the suspended crumb is passed through a filter
15 screen sized so as to recover the wet masterbatch. The material passing through the screen may be optionally recycled for further silica slurry make-up.

The wet crumb is dried such as by using forced air or fluidized bed or microwave drying techniques at a temperature between about 75° and about 135°C, preferably between about 85° and about 120°C, most preferably between about 85°
20 and about 105°C, until a suitably dry masterbatch crumb is obtained.

The dried crumb may be further processed according to industry and customer requirements.

Another advantageous application of the hydrophobicized particles is in the production of predispersions or concentrates of polymer compounding chemicals.
25 These materials typical include a chemical of interest which is predispersed in high concentrations (at least about 50 percent by weight as discussed hereinabove) in a binder, preferably a polymeric material, and are supplied in the form of pellets, slabs and the like. Thus, the polymer acts as a binder for the chemical of interest. The chemical of interest may, for example, be a silica filler, a colorant, a pigment, an
30 inorganic activator, a stabilizer and/or a flame retardant for use to produce a polymer-based product.

In a preferred embodiment of this invention the hydrophobicized particles, in the aqueous dispersion or slurry, are incorporated into a binder material, for example a polymer in the form of a polymer solution or cement. The slurry of treated particles is mixed with a hydrocarbon or other non-aqueous solution of the binder. Preferably, the solvent in which the binder is dissolved is immiscible with, or mostly immiscible with, water to form a preblend. This binder solution (e.g., polymer cement) may be made by dissolving the solid polymer in a solvent or, in the case of a solution polymer, it may be the solution resulting from the polymerisation of monomers in the solvent.

Preferably, the binder is a polymer. It will, however, be appreciated by those of skill in the art that the binder may be a quasi- or non-polymeric material such as a polyethylene wax, a rosin, a fatty acid, a high molecular weight liquid and the like, or a combination of polymer and such quasi- or non-polymeric material.

The polymer may be an elastomer (e.g., a hydrocarbon rubber), a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation, a plastic and the like.

Elastomers are well known to those of skill in the art. Non-limiting examples of suitable elastomers may be selected from the group comprising natural rubber (NR), depolymerized NR, cis-1,4-polyisoprene rubber (IR), polybutadiene rubber (BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), butyl rubber (IIR), halogenated butyl rubber (HIIR), ethylene-propylene monomer (EPM) rubber, ethylene-propylene-diene monomer (EPDM) rubber, chloroprene rubber (CR), ethylene-vinyl acetate (EVM) rubber, silicone rubber (Q), epichlorohydrin (ECO) rubber, urethane rubber (AU EU) and the like.

Plastics are well known to those of skill in the art. Non-limiting examples of suitable plastics may be selected from the group comprising polystyrene, polyethylene, polypropylene, chlorinated polyethylene, acrylonitrile-butadiene-styrene (ABS) polymers, ethylene-vinyl-acetate (EVA) plastic, polyvinyl chloride (PVC), plasticized polyvinyl chloride (PVC), polymethylmethacrylate (PMMA), epichlorohydrin (ECO) plastic and the like.

Of course those of skill in the art will recognize and appreciate that the foregoing materials may be modified with respect to parameters such as monomer sequence, monomer ratio, molecular weight (Mn, Mw, etc.), molecular weight ratio and the like while still being useful in the present invention.

5 The selection of a suitable solvent for preparation of the polymer binder solution is within the purview of a person skilled in the art and depends on the specific polymer to be dissolved. Non-limiting examples of suitable solvents may be selected from the group comprising cyclohexane, chlorobenzene, hexane, benzene, toluene, pentane and the like. Optionally, processing oil, antioxidants and other
10 chemicals known in the art as processing aids may be added to the hydrocarbon solution prior to mixing with the slurry, or they may be added after mixing the slurry and the polymer solution.

 The viscosity of the final polymer solution, sometimes referred to as a polymer cement, containing the optional ingredients, is preferably such that it closely matches
15 the viscosity of the slurry of treated particles and is generally between 1,000 and 50,000 centipoise. This may depend, at least in part on the specific gravity and/or particle size of the particles dispersed in the slurry. The temperature of the polymer solution is preferably the same as that of the slurry. Further, it is preferred to add the polymer cement in an amount such that the final dried dispersion may contain the
20 treated particulate material as the major component of the composition - i.e., the dispersion comprises at least about 50 percent by weight particulate material. Preferably, the dispersion comprises from about 50 to about 95, more preferably from about 60 to about 95, even more preferably from about 70 to about 95, percent by weight particulate material.

25 The polymer cement and, optionally, oil and antioxidants, is mixed with the slurry of treated particles until the mixture becomes homogeneous. This is confirmed by assessing the uniformity of colour and/or solids dissolution (i.e., the present of a substantially single phase although a small insubstantial amount of water may separate at this stage).

30 If not added previously, or if additional amounts are desired, oil and antioxidants may be added next and the mixing continued further until the oil and antioxidant become incorporated in the continuous phase.

Any water which separates from the preblend may be removed, discarded or recycled for slurry make-up by stopping the agitator for a suitable period and allowing the water phase to separate in the mixing tank from which it may be removed prior to proceeding with the next step. Agitation is preferably restarted after the water layer is removed.

If antioxidants and processing oil were not previously added, or if additional amounts are desired, they may be added at this stage and stirred to disperse them.

The preblend is then added to water heated to a temperature equal to, or preferably higher than the boiling point of the solvent used for the polymer cement so as to remove the solvent and produce a dispersion coagulum in the form of a crumb suspended in water. Preferably, the temperature of the water prior to addition of the preblend is in the range of from about 50°C to about 100°C, more preferably in the range of from about 90°C and to about 95°C. Further, it is preferred to add the preblend at a rate so as to maintain a temperature substantially within thereof preferred ranges. The agitation is set sufficiently high so as to maintain the crumb in a suspended state within the water, but not so high as to cause the crumb to subdivide into particles smaller than approximately 5 mm.

The solvent may be recovered from the coagulator by condensing the vapours. The material containing the suspended crumb may then be passed through a filter screen sized so as to recover the wet composition. The filtrate from this step may be optionally recycled for further slurry make-up.

The wet crumb is dried such as by using forced air or fluidized bed or microwave or other drying techniques. If microwave or other drying techniques are used, it is preferred to conduct these at a temperature in the range of from about 75°C to about 135°C, preferably in the range of from about 85°C to about 120°C, most preferably in the range of from about 85°C to about 105°C, until a suitably dry dispersion crumb is obtained.

The dried crumb may be further processed according to industry and customer requirements.

In Figure 3, there is illustrated a schematic drawing of a system suitable for carrying out the process described hereinabove. The legend in Figure 3 is as follows:

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- R1: A balance-mounted portable paint pot of nominal capacity 120 litres. The pot is equipped with a Strahman (piston) bottom valve (Vs), an oversized air-operated motor, one 6-inch radial flow agitator (top) and one 10-inch marine impeller (bottom) on a single shaft, and an external steam coil (J) for heating. The lower impeller has approximately 2 inches of clearance from the bottom of R1; the top impeller is attached at a point 9 inches higher. A valved chemical addition port (P1) is available on the removable lid and the pot may be purged with nitrogen through another port (N1) when transfer of the contents is required. A water line may be coupled to an additional port (W). A portable exhaust snorkel (E) is available in the vicinity to remove fugitive chemical emissions. R1 is used for the slurry makeup and as a vessel to carry out the above-mentioned additions to produce a slurry of hydrophobicized particles.
- T1: A nominal 500 USG glass-lined chemical reactor used for cement make-up and storage and as a mixing vessel for the slurry of treated particles and polymer cement prior to coagulation. It is equipped with a 200 rpm pneumatic drive, a marine impeller and heating jacket to speed dissolution of polymers. It has various addition ports including: M, a small manhole for introducing polymer, oil or other chemicals; P2, for solvent addition; and a nitrogen line port (N2) for pressure transfer of the contents through a large bottom drain with a valve (V2). The bottom valve is located a short distance from the tank bottom in order to reduce dead space in the piping.
- H: Armoured flex hose, 2 inch diameter, for slurry and cement transfers.

V1: A 3-way valve to control the direction of flow.

5 T2: A steam coagulator of nominal capacity 400 litres. It is equipped with a steam sparge port near the bottom and a connection to service water. An overflow port (P3) and overflow channel are situated close to the top to allow for product discharge. A large pipe at the top directs solvent vapours to a condenser (C). The tank is stirred by means of an air operated motor and an 8-inch diameter marine impeller.

10 S: A 24-inch diameter Sweco™ shaker screen (100 mesh).

C: A condenser for solvent recovery from coagulation. It is connected to cold process water through a valve (V4).

15 T3: A solvent decanter, approx. 250 USG, for recycle solvent storage and water separation. A valve (V3) allows for sampling and water discharge.

20 T4: A 60 litre plastic tank for fines settling.

G: Perforated trays for product dewatering and drying.

25 Ex: A short (24" long, 3-inch diameter screw) dewatering extruder "Rocket" powered by an explosion proof motor via a variable speed gearbox.

30 Embodiments of the present invention will be illustrated with reference to the following Example which should not be used to construe or limit the scope of the invention.

In this Example, the following materials were used.

Hi-Sil™ 233

3-chloropropyltrimethoxysilane

sodium tetrasulfide

oleylamine

5 Buna™ CB-24 (polybutadiene) cement in hexane

Sundex™ 8125

Vulcanox™ 4020

10 In a 4 L glass beaker in a fumehood were combined 510 grams of Hi-Sil 233 (amorphous precipitated silica) and 2040 grams of water and the resulting mixture was stirred with an electrically driven stirrer equipped with a radial impeller until a smooth slurry was obtained. The beaker was placed on a hot plate and the slurry was heated to 70°C while under high agitation.

15 3-Chloropropyltrimethoxysilane (41.0 gm, 206 millimoles) was added to the vortex dropwise over 10 minutes and stirring was continued for 30 minutes. Commercial distilled oleylamine (Akzo ARMEEN OLD, 1.43 grams, ~5.3 millimoles) was added to the vortex dropwise over 10 minutes. Stirring was continued for an additional 15 minutes. Sodium hydroxide solution (0.22 grams in 10 mL water) was then added dropwise to the vortex over 5 minutes. The slurry
20 viscosity increased markedly but the material was still mobile.

The above slurry was then heated to 80°C while agitation was maintained. Sodium tetrasulfide solution (38.8 grams of 34 wt% Na₂S₄ in water) was then added over 10 minutes. The colour gradually deepened from a dark yellow to a Kelly green. The slurry was stirred for an additional 4 hours at between 80-85°C. When the slurry
25 became too thick for good agitation, additional water was added as required to enable circulation to be maintained. Slurry volume was maintained at around 2500 mL. The total water added was 900 mL over the 4 hour period. After the end of the period the slurry have returned to a white colour. Commercial distilled oleylamine (Akzo ARMEEN OLD, 13.2 grams, ~49.4 millimoles) was then added dropwise to the
30 vortex over 10 minutes. Stirring was continued for 30 minutes after the end of the amine addition. Sodium hydroxide solution (2.0 grams in 50 mL of water) was then added dropwise to the vortex over 10 minutes. Considerable thickening of the slurry

was evidenced. The heat source was then removed and the slurry was allowed to cool to ambient under slow agitation. The pH of the final slurry was 8.5

When cool, the cement was quantitatively transferred to a 2,5 gallon plastic bucket in the fume hood by using a spatula and a small amount (~50 mL) of water from a wash bottle. Polybutadiene cement (3984 grams of 16 wt% Buna™ CB-24 hexane), Sundex™ 8125 aromatic process oil (191 grams) and Vulcanox™ 4020 antioxidant (5.0 grams) were then added and the mixture was stirred manually with a spatula to homogenize.

Homogenization was continued with an air stirrer for an additional 5 minutes. The mixture became extremely viscous and elastic during this time. Small beads of water which separated were crystal clear.

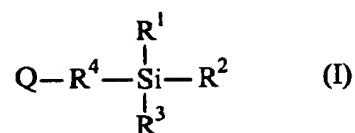
Coagulating to remove the solvent was done in a fumehood. The blend was added slowly to stirred water which was maintained at 92-95°C using low pressure steam. The aqueous coagulation serum remained almost clear throughout the coagulation although some foaming was experienced. The wet crumb was isolated by screening through a 1-mm sieve, water washed and then dried for 4 hours at 85 degrees Celsius. Product yield was 1263 grams, dry basis.

While the present invention has been described with reference to preferred embodiments and illustrative Examples, it will of course be understood by those of skill in the art that various modifications to these preferred embodiment and illustrative Examples may be made without departing from the spirit and scope of the invention.

What is claimed is:

1. A process for treating particles to render them hydrophobic, the process comprising the steps of:

(i) contacting the particles with a compound of Formula I:



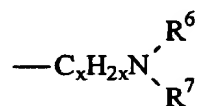
or an acid addition or quaternary ammonium salt thereof, in which:

at least one of R^1 , R^2 and R^3 are hydroxyl or hydrolysable groups;

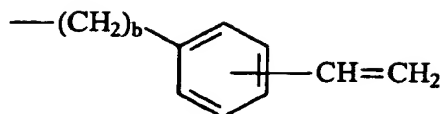
R^4 is a divalent group that is resistant to hydrolysis at the $\text{Si}-\text{R}^4$ bond;

Q is $\text{H}_2\text{N}-$ or $\text{X}-$, wherein X is an anion; and

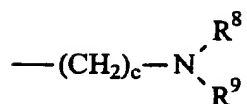
(ii) contacting the particles with: (A) a compound of formula R^5-X if Q is $\text{H}_2\text{N}-$ in Formula I, or (B) a compound of formula R^5-NH_2 if Q is $\text{X}-$ in Formula I, wherein R^5 is selected from: hydrogen; a C_{1-40} alkyl; a C_{2-40} mono-, di- or tri-unsaturated alkenyl group; a C_6-C_{40} aryl group; a group of the formula:



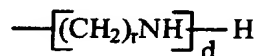
in which x is an integer from 2 to 10, R^6 and R^7 , which may be the same or different, are each selected from: hydrogen; C_{1-18} alkyl; C_{2-18} mono-, di- or tri-unsaturated alkenyl; phenyl; a group of formula:



wherein b is an integer from 1 to 10; a group of formula:

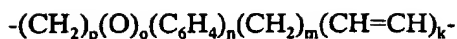


wherein c is an integer from 1 to 10, and R^8 and R^9 may be the same or different and are each selected from: hydrogen, C_{1-10} alkyl group or C_{2-10} alkenyl group, provided that there is no double bond in the position alpha to the nitrogen atom; and a group of formula:



wherein r is an integer from 1 to 6 and d is an integer from 1 to 4.

2. The process defined in claim 1, wherein each of R^1 , R^2 and R^3 is hydroxyl or a hydrolysable group.
3. The process defined in any one of claims 1-2, wherein the hydrolysable group has the formula $\text{OC}_p\text{H}_{2p+1}$, where p has a value from 1 to 10.
4. The process defined in any one of claims 1-3, wherein divalent group R^4 has the formula:



in which k, m, n, o and p are all whole numbers and the order of the moieties is not restricted other than neither N nor O is directly bound to Si in the compound of Formula I.

5. The process defined in any one of claims 1-4, wherein R⁵ is a C₈₋₂₀ monounsaturated alkenyl group.
6. The process defined in any one of claims 1-4, wherein R⁵ is a C₁₆₋₁₈ monounsaturated alkenyl group.
7. The process defined in any one of claims 1-6, wherein R⁶ is hydrogen.
8. The process defined in any one of claims 1-7, wherein R⁵ is hydrogen and R⁶ is an alkenyl group selected from the group consisting of soya alkyl, tall oil alkyl, stearyl, tallow alkyl, dihydrogenated tallow alkyl, cocoalkyl, rosin alkyl, palmityl and derivatives of these which include one or more unsaturations.
9. The process defined in any one of claims 1-8, wherein X is selected from the group consisting of acetate, chlorine, bromine, iodine and sulphate.
10. The process defined in any one of claims 1-9, the particles comprise inorganic water insoluble compounds.
11. The process defined in any one of claims 1-9, wherein the particles are selected from the group consisting of titanium oxide, ferric oxide, hydrated ferric oxide, ferrous oxide, antimony oxide, barium carbonate, zinc oxide, zinc borate, lead oxide (including red lead oxide), dibasic lead phosphite, lead silicate, tribasic lead sulfate and mixtures thereof.

12. The process defined in any one of claims 1-9, wherein the particles comprise silica.
13. The process defined in any one of claims 1-12, comprising the further step of: admixing the treated particles with a polymer solution and forming the mixture into a polymer dispersion.
14. The process defined in any one of claims 1-12, comprising the further step of: admixing a slurry of treated particles with a polymer solution and forming the mixture into a polymer dispersion.
15. The process defined in any one of claims 13-14, wherein the polymer solution comprises a polymer and a solvent.
16. The process defined in claim 15, wherein the polymer is selected from the group consisting of an elastomer, a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation, a plastic and mixtures thereof.
17. The process defined in claim 16, wherein the elastomer is selected from the group consisting of natural rubber (NR), cis-1,4-polyisoprene rubber (IR), polybutadiene rubber (BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), butyl rubber (IIR), halogenated butyl rubber (HIIR), ethylene-propylene monomer (EPM) rubber, ethylene-propylene-diene monomer (EPDM) rubber, chloroprene rubber (CR), ethylene-vinyl acetate (EVM) rubber, silicone rubber (Q), epichlorohydrin (ECO) rubber, urethane rubber (AU EU) and mixtures thereof.
18. The process defined in claim 16, wherein the plastic is selected from the group consisting of polystyrene, polyethylene, polypropylene, chlorinated polyethylene, acrylonitrile-butadiene-styrene (ABS) polymers, ethylene-vinyl-acetate (EVA) plastic, polyvinyl chloride (PVC), plasticized polyvinyl chloride (PVC),

polymethylmethacrylate (PMMA), epichlorohydrin (ECO) plastic and mixtures thereof.

19. The process defined in claim 15, wherein the solvent is substantially immiscible with water.

20. The process defined in claim 15, wherein the solvent is selected from the group consisting of cyclohexane, chlorobenzene, hexane, benzene, toluene, pentane and mixtures thereof.

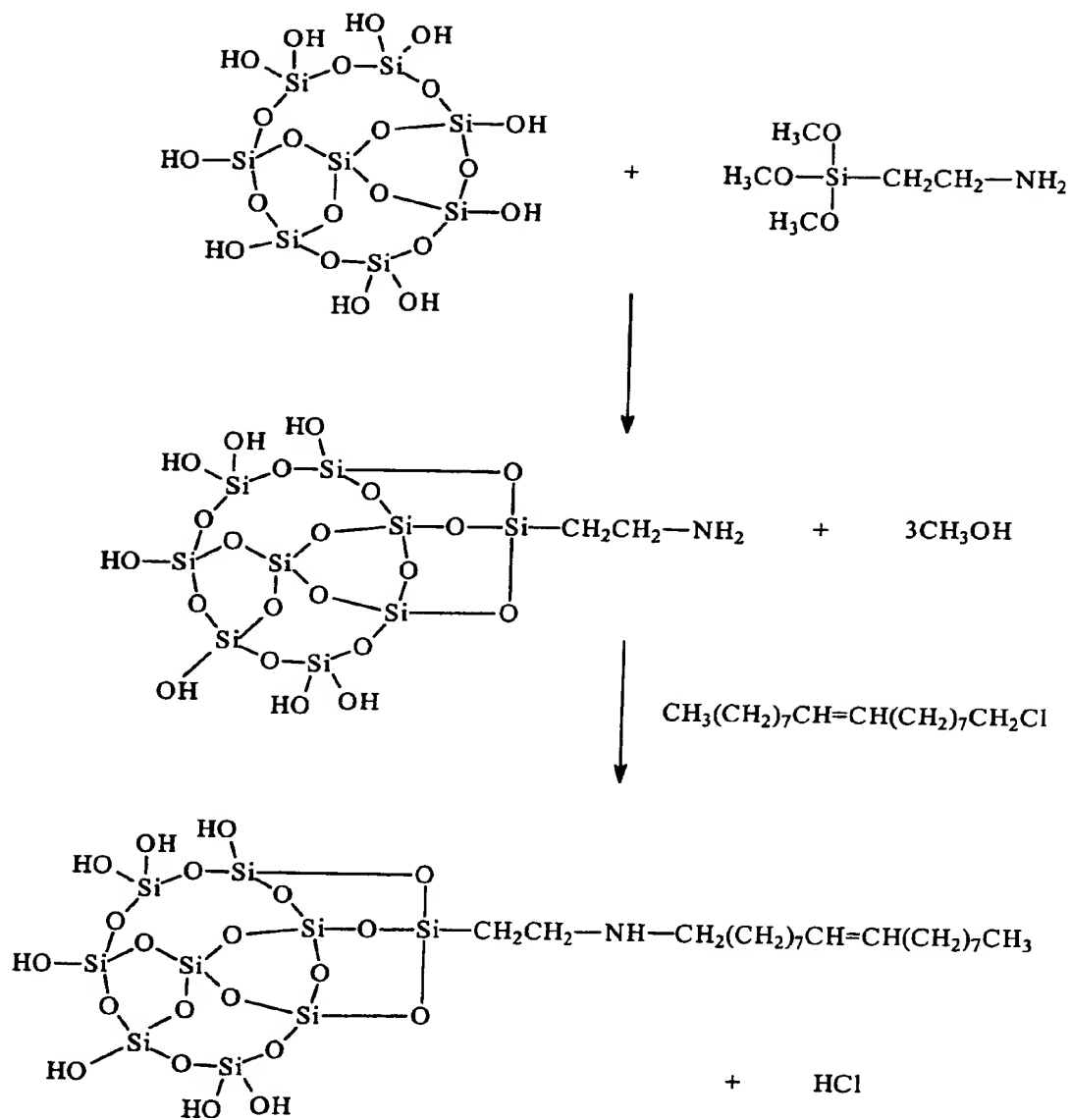


FIG. 1

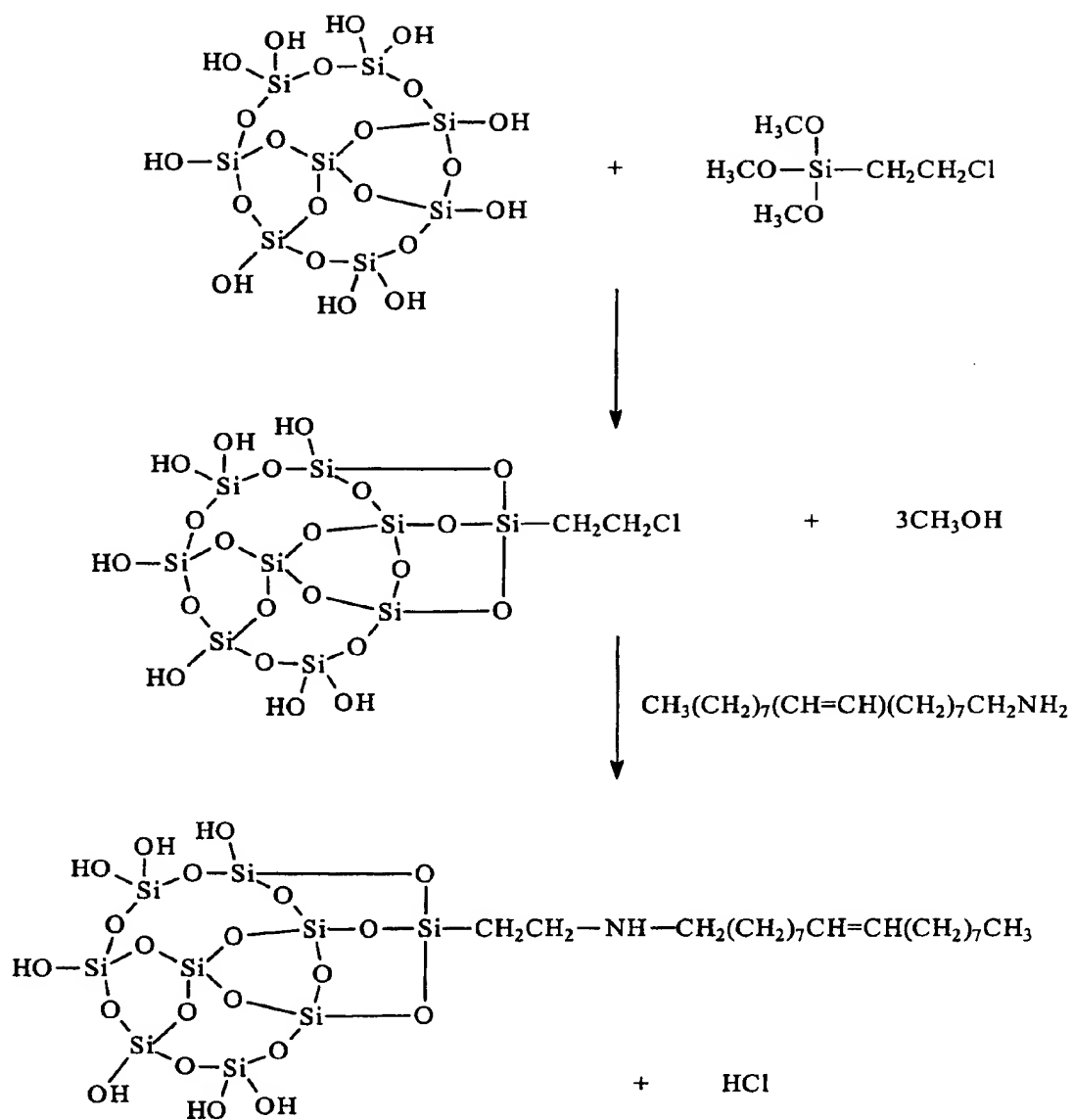


FIG. 2

FIG. 3

